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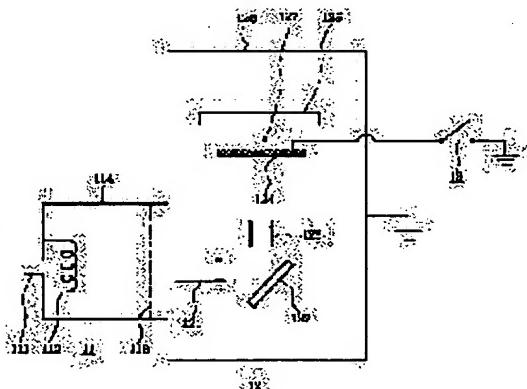
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(54) ION BEAM SPUTTERING DEVICE, PRODUCTION OF SEMICONDUCTOR DEVICE AND PRODUCTION OF PHOTOELECTRIC CONVERTER

(57)Abstract:

PROBLEM TO BE SOLVED: To prevent bad influence on semiconductor layer by ion beam sputtering and to produce an excellent semiconductor device.

SOLUTION: This ion sputtering device has a primary means 11 of generating an ion beam and orientating the ion beam 121 toward a prescribed direction, a secondary means of holding a target 122 in a position to be irradiated with the ion beam so that the target 122 is sputtered by the irradiation of the ion beam orientated toward the prescribed direction, a third means of holding an electrically conductive substrate 124 provided with a semiconductor thin coating layer for depositing the sputtered target components and a fourth means of setting the electric potential of the electrically conductive substrate to non-earth one.



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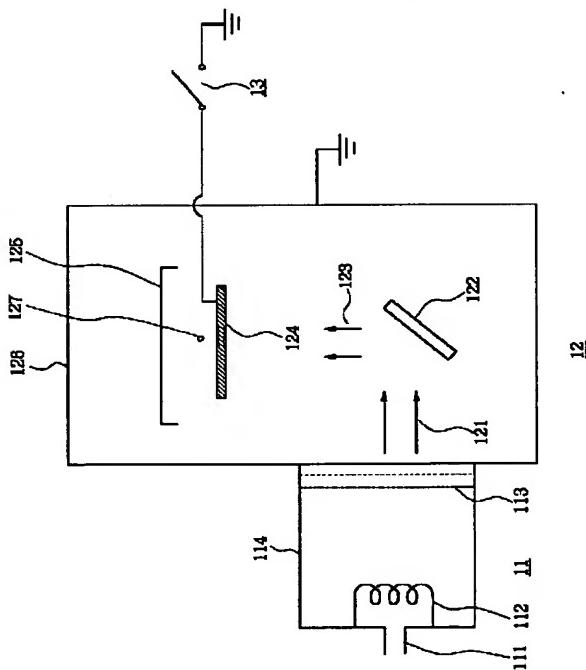
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(54) 【発明の名称】イオンビームスペッタ装置、半導体装置の製造法及び光電変換装置の製造法

(57) 【要約】

【課題】 イオンビームスパッタによって半導体層が受ける悪影響を防止し、優れた半導体装置を製造する。

【解決手段】 a. イオンビームを発生させ、該イオンビームを所定方向に向ける第1の手段、b. 前記所定方向に向けたイオンビームの照射によって該ターゲットがスペッタされるように、該イオンビームの照射を受ける位置において該ターゲットを保持する第2の手段、c. 前記スペッタされたターゲット成分を堆積させるための半導体薄膜層を設けた導電性基板を保持する第3の手段、d. 前記導電性基板の電位を非アース電位に設定する第4の手段、を有するイオンビームスペッタ装置、及び該装置を用いた半導体装置の製造法、並びに光電変換装置の製造法を提供する。



【特許請求の範囲】

- 【請求項1】 a. イオンビームを発生し、該イオンビームを所定方向に向ける第1の手段、
 b. 前記所定方向に向けたイオンビームの照射によってターゲットがスペッタされるように、該イオンビームの照射を受ける位置において該ターゲットを保持する第2の手段、
 c. 前記スペッタされたターゲット成分を堆積させるための半導体薄膜層を設けた導電性基板を保持する第3の手段、
 d. 前記導電性基板の電位を非アース電位に設定する第4の手段、を有するイオンビームスペッタ装置。

【請求項2】 前記導電性基板は、長尺状導電性基板である請求項1に記載のイオンビームスペッタ装置。

【請求項3】 前記第4の手段は、前記導電性基板とアースとを絶縁する手段を有する請求項1に記載のイオンビームスペッタ装置。

【請求項4】 前記第4の手段は、前記導電性基板のアースに対する電位が前記薄膜半導体層表面のアースに対する電位と同一極性に設定されるように、該導電性基板に電圧を印加する手段を有する請求項1に記載のイオンビームスペッタ装置。

【請求項5】 前記電圧は、-100ボルト以上0ボルト未満に設定されている請求項4に記載のイオンビームスペッタ装置。

【請求項6】 前記薄膜半導体層は、半導体接合をもつ半導体層である請求項1に記載のイオンビームスペッタ装置。

【請求項7】 前記薄膜半導体層は、非単結晶シリコンによって形成された半導体接合をもつ半導体層である請求項1に記載のイオンビームスペッタ装置。

【請求項8】 前記薄膜半導体層は、アモルファスシリコン、微結晶シリコン又は多結晶シリコンによって形成されたp i n接合、n i p接合、p n接合又はn p接合をもつ半導体層である請求項1に記載のイオンビームスペッタ装置。

【請求項9】 a. イオンビームスペッタ装置内のイオンビームが照射される位置にターゲットを配置する工程、
 b. 前記イオンビームスペッタ装置内の前記ターゲットから発生するターゲット成分が堆積する位置に薄膜半導体層を設けた導電性基板を配置する工程、

c. イオンビームを発生し、該イオンビームを所定方向に向けることにより、前記ターゲットに該イオンビームを照射し、該ターゲットをスペッタし、前記ターゲット成分を前記薄膜半導体層上に堆積させる工程、を有する半導体装置の製造法であって、
 少なくとも前記ターゲット成分が堆積する期間中には前記導電性基板が非アース電位になるように、前記導電性基板の電位を設定することを特徴とする半導体装置の製

造法。

【請求項10】 前記導電性基板は、長尺状導電性基板である請求項9に記載の半導体装置の製造法。

【請求項11】 前記導電性基板とアースとを絶縁することにより、前記導電性基板の電位を設定する請求項9に記載の半導体装置の製造法。

【請求項12】 前記導電性基板のアースに対する電位が前記薄膜半導体層表面のアースに対する電位と同一極性に設定されるように、該導電性基板に電圧を印加する請求項9に記載の半導体装置の製造法。

【請求項13】 前記電圧は、-100ボルト以上0ボルト未満に設定する請求項12に記載の半導体装置の製造法。

【請求項14】 前記薄膜半導体層は、半導体接合をもつ半導体層である請求項9に記載の半導体装置の製造法。

【請求項15】 前記薄膜半導体層は、非単結晶シリコンによって形成された半導体接合をもつ半導体層である請求項9に記載の半導体装置の製造法。

20 【請求項16】 前記薄膜半導体層は、アモルファスシリコン、微結晶シリコン又は多結晶シリコンによって形成されたp i n接合、n i p接合、p n接合又はn p接合をもつ半導体層である請求項9に記載の半導体装置の製造法。

【請求項17】 前記ターゲット成分の堆積により透明導電膜を形成する請求項9に記載の半導体装置の製造法。

【請求項18】 a. イオンビームスペッタ装置内のイオンビームが照射される位置にターゲットを配置する工程、
 b. 前記イオンビームスペッタ装置内の、前記ターゲットから発生するターゲット成分が堆積する位置に薄膜半導体層を設けた導電性基板を配置する工程、

c. イオンビームを発生させ、該イオンビームを所定方向に向けることにより、前記ターゲットに該イオンビームを照射し、該ターゲットをスペッタし、前記ターゲット成分を前記薄膜半導体層上に堆積させる工程、を有する半導体装置の製造法であって、
 少なくとも前記ターゲット成分が堆積する期間中には前記導電性基板が非アース電位になるように、前記導電性基板の電位を設定することを特徴とする光電変換装置の製造法。

40 【請求項19】 前記導電性基板は、長尺状導電性基板である請求項18に記載の光電変換装置の製造法。
 【請求項20】 前記導電性基板とアースとを絶縁することにより、前記導電性基板の電位を設定する請求項18に記載の光電変換装置の製造法。

【請求項21】 前記導電性基板のアースに対する電位が前記薄膜半導体層表面のアースに対する電位と同一極性に設定されるように、該導電性基板に電圧を印加する

請求項18に記載の光電変換装置の製造法。

【請求項22】前記電圧は、-100ボルト以上0ボルト未満に設定する請求項21に記載の光電変換装置の製造法。

【請求項23】前記薄膜半導体層は、半導体接合をもつ半導体層である請求項18に記載の光電変換装置の製造法。

【請求項24】前記薄膜半導体層は、非単結晶シリコンによって形成された半導体接合をもつ半導体層である請求項18に記載の光電変換装置の製造法。

【請求項25】前記薄膜半導体層は、アモルファスシリコン、微結晶シリコン又は多結晶シリコンによって形成されたp i n接合、n i p接合、p n接合又はn p接合をもつ半導体層である請求項18に記載の光電変換装置の製造法。

【請求項26】前記ターゲット成分の堆積により透明導電膜を形成する請求項18に記載の光電変換装置の製造法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、太陽電池、ライン光センサー若しくはエリア光センサーなどの光電変換装置、又は薄膜トランジスタを構成する薄膜半導体層、特にアモルファスシリコン、微結晶シリコン又は多結晶シリコンなどの非単結晶シリコンによって形成させたp i n接合層、n i p接合層やp n接合層等の半導体接合層を持つ薄膜半導体層上に、導電膜を成膜するための改善されたイオンビームスパッタ装置、並びに半導体装置及び光電変換装置の製造法に関するものである。

【0002】

【従来の技術】薄膜半導体は、導電膜を設けた基板の上に薄膜半導体層を設けた後、該薄膜半導体層上に導電膜を成膜して、素子化される。例えば、上述の光起電力素子等の光電変換装置は、導電性表面をもつ基板上に上述したような薄膜半導体層を設け、さらに該薄膜半導体層上に透明導電膜が成膜される。

【0003】従来、透明導電膜などの導電膜は、蒸着法やDCマグネットロンスパッタ法によって、薄膜半導体層の上に形成されていた。

【0004】例えば導電性基板上に反射層を介して半導体層が形成され、さらにその上に透明導電膜が形成されている光起電力素子において用いられる該透明導電膜の材料としては、通常In₂O₃、SnO₂、ZnO、ITO（インジウム錫酸化物）などが知られており、その形成方法としては、真空蒸着法、スパッタ法、CVD法、スプレー法などがある。この中でも特にITO透明導電膜は、その透過率、導電性、エッチング特性に優れており最もよく用いられている。このITO膜の形成方法としては、形成された膜の特性の面からの優位性、および生産性の面での優位性からDCマグネットロンスパッタ法が

広く用いられている。

【0005】上記光起電力素子が効率よく起電力を発生するためには、より低抵抗で、より透過率が高い透明導電膜が要求される。しかしながら、例えば、成膜時の基板温度を比較的低い230°C以下程度として、量産性に優れた堆積速度10Å/sec.以上程度で、導電性基板／反射層／半導体層上の透明導電膜として適した厚みである500Å～1000Å程度の透明導電膜を形成した場合には、シート抵抗がせいぜい50Ω/□程度の透明導電膜しかえられない。

【0006】また、特開平7-331413号公報に記載されたイオンビームスパッタによる透明導電膜の成膜方法が提案されている。上述の公開明細書の記載によれば、半導体層として、ホモ接合CuInSe₂などの特殊な化合物半導体が使用されている。しかしながら該方法を例えばアモルファスのn i p接合を有する薄膜半導体層上の導電膜形成に適用するにあたって、以下のような課題があることが、本発明者の実験により明らかになった。

【0007】即ち本発明者の実験によれば、光起電力素子を形成させる導電性基板上の薄膜半導体層の上に、イオンビームスパッタによって、透明導電膜などの導電膜を成膜した時、該導電性基板から該薄膜半導体層の表面に向かって、直流電流（この電流は、薄膜半導体層の表面から導電性基板への負電荷の流れによるものと推定される）が流れ、この結果、該薄膜半導体層の電気的に弱い部分（周囲と比較して低抵抗な箇所）に電流が集中して流れ、その箇所に破壊（ショート）を引き起こすこと、が判明した。このため、光起電力素子としての機能は、低下してしまい、更に長期間の使用における経時安定性を悪化させていた。

【0008】上述した実験に基づく本発明者の知見によれば、上述のショートの原因は、以下のとおりであることが判明した。すなわち、特に、導電性基板として、ロール状ステンレススチールを使用し、この上に、ロール状に薄膜半導体層を設けた後で、該薄膜半導体層の上にイオンビームスパッタによって透明導電膜を成膜した時、ロール状ステンレススチールを支持するための支持部や搬送を安定化させるための支持ロール等が金属などの導電部材によって構成されているため、これらとの間での接触によって、ロール状ステンレススチールが結果的にアースされてしまい、このためイオンビームスパッタ時に、薄膜半導体層表面側の電位と導電性基板のアース電位との間に電界が生じ、この電界が薄膜半導体層に印加され、電流が該薄膜半導体層内に存在している低抵抗箇所を通して導電性基板から半導体層表面に向かって集中的に流れること、であった。

【0009】イオンビームスパッタは、DCマグネットロンスパッタ等と比較してプラズマのエネルギーが強い。従って、上記電流による光起電力素子の機能低下はより

大きな問題となる。さらに半導体層に与えられるプラズマダメージも問題となる。

【0010】

【発明が解決しようとする課題】本発明の目的は、上述のショートの発生を抑制した改善されたイオンビームスパッタ装置、並びに半導体装置及び光電変換装置の製造法を提供することにある。

【0011】更には、本発明の別の目的は、イオンビームスパッタ時のイオンによる半導体層へのプラズマダメージを軽減し、大量生産に適したロール状の導電性基板を連続搬送することを可能にした、改善されたイオンビームスパッタ装置、並びに半導体装置及び光電変換装置の製造法を提供することにある。

【0012】また、本発明のもう一つの目的は、粒径の大きさが均一で、粒子の分布が密で、低抵抗で、高透過率で、耐酸性・耐アルカリ性に優れ、かつ、耐熱性に優れ、長期の使用に対して安定な透明導電膜を形成することを可能にしたイオンビームスパッタ装置並びに該透明導電膜を設けた半導体装置及び光電変換装置の製造法を提供することにある。

【0013】

【課題を解決するための手段】本発明は、

- イオンビームを発生し、該イオンビームを所定方向に向ける第1の手段、
- 前記所定方向に向けたイオンビームの照射によってターゲットがスパッタされるように、該イオンビームの照射を受ける位置において該ターゲットを保持する第2の手段、
- 前記スパッタされたターゲット成分を堆積させるための半導体薄膜層を設けた導電性基板を保持する第3の手段、
- 前記導電性基板の電位を非アース電位に設定する第4の手段、を有するイオンビームスパッタ装置を提供するものである。

【0014】

また、本発明は、

- イオンビームスパッタ装置内のイオンビームが照射される位置にターゲットを配置する工程、
- 前記イオンビームスパッタ装置内の前記ターゲットから発生するターゲット成分が堆積する位置に、薄膜半導体層を設けた導電性基板を配置する工程、
- イオンビームを発生し、該イオンビームを所定方向に向けることにより、前記ターゲットに該イオンビームを照射し、該ターゲットをスパッタし、前記ターゲット成分を前記薄膜半導体層上に堆積させる工程、を有し、少なくとも前記ターゲット成分が堆積する期間中には前記導電性基板が非アース電位になるように、前記導電性基板の電位を設定することを特徴とする半導体装置の製造法及び光電変換装置の製造法を提供するものである。

【0015】

【発明の実施の形態】

(透明導電膜をイオンビームスパッタ形成する装置) 図1は、本発明に係る透明導電膜をイオンビームスパッタ形成するイオンビームスパッタ装置の一例を示す概略構成図である。

【0016】図1において、本発明の装置は、アルゴンガス導入管111、導入されたアルゴンガスをイオンに励起するイオン化ヒータ112、及び発生イオンをビーム状に加速させ、所定方向に出射させる加速器113を真空室114内に備えたイオンビーム発生装置11、前記所定方向のイオンビーム121の照射を受ける位置に配置され、該イオンビーム121の照射によってスパッタされるターゲット122、前記スパッタされたターゲット成分123を堆積させるために配置した図4に図示する下述の薄膜半導体層41を設けた導電性基板124、該導電性基板124を加熱する基板加熱用ヒータ125及び温度制御用の熱電対127を真空室126内に備えた堆積室12、並びに前記ターゲット成分123の堆積期間中に、前記導電性基板124をアースに対して電気的に絶縁するためにオープンに設定したスイッチ13を有するイオンビームスパッタ装置である。該スイッチ13のオープンによって、前記導電性基板124とアース電位との間は絶縁され、薄膜半導体層41の上に下述の図4に図示する透明導電膜42の成膜が実施される。

【0017】図2は、本発明装置の別の態様を図示している。図2に図示した装置は、アルゴンガス導入管111、導入させたアルゴンガスをイオンに励起させるイオン化ヒータ112、及び発生イオンをビーム状に加速させ、所定方向に出射させる加速器113を真空室114内に備えたイオンビーム発生装置11、前記所定方向のイオンビーム121の照射を受ける位置に配置し、該イオンビーム121の照射によってスパッタされるターゲット122、前記スパッタされたターゲット成分123を堆積させるために配置した図4に図示する薄膜半導体層41を設けた導電性基板124、該導電性基板124を加熱する基板加熱用ヒータ125及び温度制御用の熱電対127を真空室126内に備えた堆積室12、並びに前記ターゲット成分123の堆積期間中に、前記導電性基板124をアースに対して-100ボルト以上0ボルト未満の範囲に設定する電圧印加手段21を有するイオンビームスパッタ装置である。

【0018】また、本発明の別の具体例では、導電性基板124は、不図示のアルミナでできた絶縁碍子の基板ホルダーに固定し、これにより導電性基板124は、真空室126等のアース電位に対して電気的に絶縁することができる。

【0019】図2における電圧印加手段21は、イオンビームスパッタ期間中に於いて、前記薄膜半導体層41表面の電位状態がアースに対して、マイナス電位であることに基づいて、前記導電性基板124をアースに対し

て-100ボルト以上0ボルト未満の範囲、好ましくは、-60ボルト以上0ボルト未満の範囲、特に好ましくは、-40ボルト以上0ボルト未満の範囲の電圧を印加することができる。この結果、薄膜半導体層41の上に下述の図4に図示する透明導電膜42が成膜される。

【0020】また、本発明者の実験によれば前記電圧印加手段21による前記導電性基板124に印加される電圧が、-100ボルトを越えてマイナス側に大きくなると、半導体層41表面へのプラズマダメージが発生することが判明した。

【0021】図3は、本発明の別の態様を図示したものである。図3において、ロール状ステンレススチールなどの金属製ロール体によって成形されているロール状導電性基板31は、矢標32の方向に沿って連続的に又はステップ的に搬送される。このロール状導電性基板31の先端部は、真空状態に設定された基板搬入室33内の軸受け(図示せず)によって固定され、巻き取りロール331に巻きとられる。一方、ロール状導電性基板31の後端部は、真空状態に設定された基板搬出室34の軸受け(図示せず)によって固定され、予め送り出しロール341に巻かれている。基板搬出室34及び基板搬入室33内にはそれぞれの軸受けを駆動する駆動源(図示せず)が設けられ、また水平方向に移動中のロール状導電性基板31の張力を一定にする送りロール332及び342が設けられている。堆積室35と基板搬入室33との間、及び堆積室35と基板搬出室34との間は不図示のガスゲートによって結ばれており、基板31が大気に触れないようになっている。

【0022】本発明で用いるロール状導電性基板31としては、好ましくは、該ロール状導電性基板31の上に、例えば特開昭57-43413号公報、特開平4-299823号公報等に記載されたロール・ツ・ロール方式及びその装置を用いることによって、図4に図示する下述の薄膜半導体層41が設けられている。

【0023】本発明で用いたロール・ツ・ロール方式及びその装置は、ロール状導電性基板の連続搬送中に、該ロール状導電性基板をガスゲート手段等の不拡散接合手段によって独立させた複数の成膜室を通過させることによって、アモルファスシリコン、微結晶シリコン又は多結晶シリコンなどの非単結晶シリコンによって形成させたp i n接合層、n i p接合層やp n接合層等の半導体接合層を持つ薄膜半導体層をロール状導電性基板の上に連続的に成膜する方法及びその装置である。

【0024】この薄膜半導体層41が設けられているロール状導電性基板31は、イオンビーム発生装置(図示せず)及び堆積室35からなるイオンビームスパッタ装置の堆積室35内において、薄膜半導体層41の上に透明導電膜42の成膜が実施される。イオンビーム発生装置及び堆積室35は、上述の図1及び2に図示した実施例で用いたものと同様のものを用いることができる。

【0025】図3に図示する装置において、ターゲット351のスペッタにより生じたターゲット成分352の堆積期間中に、前記導電性基板31をアースに対して電気的に絶縁するために、本例では導電性基板31と接触する各ロール341、342、331及び332の表面に、両面テープで絶縁性ポリイミドフィルム(図示せず)を予め貼っている。これにより導電性基板31は、アースに接続させたイオンビームスパッタ装置35等の電位に対して絶縁された。電気的絶縁手段としては、上述の他に、テフロン等の樹脂、紙等からなる絶縁物質を各ロール341、342、331及び332の表面に、貼り付けても良い。また、各ロール341、342、331及び332の表面に、ペンキ等の絶縁物質を塗布しても良い。また、各ロール341、342、331及び332の表面にテフロン等の樹脂を含浸させても良い。更には、各ロール341、342、331及び332の回転軸の軸受け(図示せず)として、テフロン、デルリン等の樹脂製のものを用いても良い。また、これらの手段をいくつか組み合わせても良い。

【0026】また、図3に図示する装置において、ターゲット成分352の堆積期間中に、前記導電性基板31を非アース電位に接続することができる。この際の電圧印加手段21による導電性基板31への印加電圧は、イオンビームスパッタ時に発生する導電性基板とアース電位との間のセルフ・バイアス電位と同電位の-100ボルト以上0ボルト未満の範囲に設定するのが良い。この電圧印加手段からの電圧は、直流電圧に限定されるものではなく、交流電圧、RF電圧等を直流電圧に重畠してもよい。

【0027】上記図1、図2及び図3に図示の実施例におけるイオンビームスパッタ装置のイオンビーム発生には、熱陰極電子衝撃のイオン源を用いることができる。発生したイオンビームは、堆積室12又は35内に、イオンビームに対して斜めに配置されたターゲットに入射し、ターゲットをスパッタする。ターゲットとしては例えばITOのペレット(例えばIn₂O₃が90wt% - SnO₂が10wt%の混合焼結体)を用いることができる。ペレットの相対密度は65%以上であればよく、好ましくは70%以上、更に好ましくは80%以上のがよい。

【0028】上記したターゲットの材料としては、ITO以外にSnO₂、In₂O₃、ZnO等を用いてもよい。また、上述したような酸化物を用いたターゲットのかわりに、例えばInSnやZnの金属ペレットを用い、酸素を反応ガスとして用い、これによって透明導電性酸化膜を成膜することができる。

【0029】また、透明導電膜42を堆積している期間中に、導電性基板124又は31と堆積室12又は35との間の電圧が上記セルフバイアスVselfとして電圧計50によって測定される。セルフバイアス電圧(Vself)は

、 $-100 \text{ V} \leq V_{self} < 0 \text{ V}$ となるようにスパッタ条件(イオンビーム電流(好ましくは1A~500A)、成膜圧力(好ましくは 3×10^{-6} ~ 1×10^{-2} Torr)、酸素分圧(好ましくは0~ 5×10^{-4} Torr)、導電性基板とターゲット間の距離(好ましくは50mm~800mm)、イオンの引き出し電圧(好ましくは0.2~30kV)等)を選んでやるとよい。イオンによる半導体層へのプラズマダメージをより軽減するために V_{self} は好ましくは $-60 \text{ V} < V_{self} < 0 \text{ V}$ 、更に好ましくは $-40 \text{ V} < V_{self} < 0 \text{ V}$ となるようにスパッタ条件(イオンビーム電流、成膜圧力、基板とターゲット間の距離、イオンの引き出し電圧等)を選んでやるとよい。

【0030】また、本発明の装置では、導電性基板124又は31を成膜期間中に加熱するための基板加熱用ヒータ125としては、シーズヒータや赤外線ランプ等を用いることができ、導電性基板124または31の直上に設置した熱電対127の指示値が一定となるように制御する。

【0031】本発明で用いる導電性基板31としては、厚さ0.2mm、50mm角のステンレス板(sus430)の表面を不活性ガス中において焼鈍処理するBA(ライト・アニール；光輝焼鈍)処理したものや、厚さ0.2mm、巾360mm、長さ300mのステンレス・ロール(sus430)の表面をBA処理したものを用いることができるが、本発明においてはこれらのものには限定されない。表面処理としては、上記BA処理に限定されるものではなく、例えば冷間圧延後、熱処理及び酸洗処理によって表面に凹凸状の筋を形成させたことによる粗面化したもの(例えば、No.2D鋼板)を用いることができる。また、導電性基板31としては、上記ステンレス板(ロール)の他に、亜鉛鋼板、アルミニウム板(ロール)、メッキ鋼板(ロール)や金属メッキしたプラスチックフィルム(テープ)等も使用できる。

【0032】本発明で用いる導電性基板124又は31の表面には、アルミニウム膜、銀膜、ニッケル膜や銅膜などの金属膜で形成した反射層43が設けられていてよい。該反射層43の上には、酸化亜鉛膜、ITO膜などの透明導電膜44が堆積されていてよい。これらの反射層43及び下地透明導電膜44は、DCマグネットロンスパッタ法によって成膜されるのが好ましい。

【0033】本発明で用いる導電性基板124上の薄膜半導体層41は、p-i-n接合を持ったセルを複数、例えばタンデム又はトリプル素子とすることができる。例えば、本発明において好ましく用いられる光起電力素子用の半導体層は、プラズマCVD法で形成される。すなわち、材料ガスとしてSiH₄、PH₃、H₂を用い、電力を投入し、n型半導体層419としてn型a-Si層を、さらにSiH₄、GeH₄、H₂を用い、i型半導体層418としてi型a-SiGe層を、続いてSiH₄、BF₃、H₂を用い、p型半導体層417としてp

型μc(微結晶)-Si層を順次形成した第1番目のn-i-pセルを設け、続いて2層目のセルとしてn型半導体層416、i型半導体層415及びp型半導体層414を持つ第2番目のセルを積層し、更に、第3番目のn型半導体層413、上記i型a-SiGe層をi型a-Si層に変更した半導体層であるi型半導体層412及びp型半導体層411を持つ第3番目のセルを積層し、この第3番目のセルをトップセルとして積層したトリプル型光起電力素子用の半導体層が挙げられる。この薄膜半導体層41は、アモルファス、微結晶又は多結晶に制限されるものではない。また、n-i-pを重ねる回数は1以上であればよい。さらに、薄膜半導体層41としては、n-i-p接合の構成に限定されるものではなくp-in接合やpn接合、np接合等の各種接合体であっても良い。

【0034】(透明導電膜をイオンビームスパッタ形成する方法)以下、図1に図示した装置を用いて透明導電膜を形成する方法を作製手順にしたがって説明する。

【0035】まず、初めに、基板124を碍子製基板ホルダー(図示せず)に装着し、導電性基板124と堆積室12との間の電気抵抗をテスターで測定することにより、基板124が電気的にアースに対して絶縁されていることを確認した。この時の抵抗値は、高ければ高いほど流れる電流を少なくすることができるため好ましいが、300kΩ以上あれば良く、好ましくは600kΩ以上、更に好ましくは800kΩ以上あれば良い。

【0036】次に、室114を真空ポンプ(図示せず)で適当な真空度まで減圧し、高真空室114とした後、該高真空室114内にアルゴンガスを導入した。また、この時、導電性基板124をヒータ14で所定の温度に加熱した。

【0037】その後、電源(図示せず)により、イオンガンのイオンビーム電流とイオンの引き出し電圧等を、アルゴン流量および/または排気バルブの開度の調節し、これにより成膜圧力を調整し、所望のセルフバイアス電圧を維持しながら、基板124の表面すなわち薄膜半導体層41の上に、透明導電膜42を所望の膜厚になるよう形成した。

【0038】(実施例1) 本実施例では、図2に図示の装置を用いた。この際、導電性基板124上には、予めプラズマCVD法を用い、n型アモルファシリコン層(10nm)、i型アモルファシリコンゲルマニウム層(200nm)、p型微結晶シリコン層(5nm)、n型アモルファシリコン層(10nm)、i型アモルファシリコンゲルマニウム層(100nm)、p型微結晶シリコン層(5nm)、n型アモルファシリコン層(10nm)、i型アモルファシリコン層(70nm)、p型微結晶シリコン層(5nm)を順に堆積することによりトリプルセルを設けた。導電性基板124とアース間との電圧 V_0 を-120ボルト $\leq V_0 \leq +20$ ボ

ルトの範囲である下記11ポイントの電圧に変化させ、透明導電膜を形成し、それぞれの透明導電膜が設けられ、下記手順(1)～(5)に従って、11種の光起電力素子(太陽電池として機能する素子)を作製した。

【0039】11ポイントの電圧値として、+20ボルト、+5ボルト、0ボルト(アース)、-5ボルト、-20ボルト、-40ボルト、-60ボルト、-80ボルト、-100ボルト、-100ボルト及び-120ボルトを選択した。

【0040】(1) 導電性基板124は、アルミナでできた絶縁碍子の基板ホルダー(図示せず)に固定した。(2) 導電性基板124と堆積室12との間の電気抵抗をテスターで測定したところ抵抗値はMΩ台を示し、確かに基板124が電気的にアースに対して絶縁されていることを確認した。

(3) 真空ポンプ(図示せず)で真密度が 10^{-6} Torr台になるまで室114の内を排気し、高真密度室114とした後、この室114内にガス導入管111よりアルゴン*

*ガスを導入した。

(4) ヒータ125は、熱電対15の指示値が190°Cになるように出力制御した。なお、膜厚はおおむね700Åとなるようにした。

(5) 電源(図示せず)によりイオンガンのイオンビーム電流とイオンの引き出し電圧等を、アルゴン流量および/または排気バルブの開度調節により成膜圧力を下記表1のとおり調整することにより、導電性基板124と堆積室12との間でのセルフバイアス電圧Vselfを-120ボルト≤Vself<0ボルトの範囲内の表1に記載のとおり設定した。また、成膜中にフローティングを短絡させ、Vself=0ボルトでの成膜もおこなった。更には、直流電源を用いて、導電性基板124への印加電圧V。を0ボルト<V。≤+20ボルトの範囲で印加しながらの成膜もおこなった。

【0041】

【表1】

表 1

セルフ・バイアス電圧(ボルト)	成膜圧力(Torr)
-120	1×10^{-6}
-110	2×10^{-6}
-100	3×10^{-6}
-80	5×10^{-6}
-60	8×10^{-6}
-40	2×10^{-4}
-20	5×10^{-4}
-5,0,+5,+20	5×10^{-3}

【0042】こうして作成した光起電力素子の2001lux(ルックス)の蛍光灯下での開放電圧の測定結果を図5に示す。

【0043】更に、上述した11種の太陽電池の透明導電膜42の表面に、銀ペーストをスクリーン印刷して集電電極を形成し、AM1.5(100mW/cm²)の光照射下にて得られた光電変換効率を図6に示す。

【0044】図5及び図6から電圧が0(アース)ボルト～+10ボルトの場合では、光起電力素子の機能が著しく低下するのが分かる。これは半導体層41表面に発生する負電荷が半導体層41から導電性基板124側に向かって流れる際に、半導体層41の電気的に弱い部分に集中して流れ、その部分に破壊(ショート)を引き起こすためと思われる。

【0045】また、セルフバイアス電圧がマイナス側に大きくなり過ぎると(-100ボルトを越えて、よりマイナス側に大きくなる場合)、光起電力素子の機能は低下する。特に、低照度での開放電圧の低下が著しい。この原因は、飛来してくるイオンによる半導体層41へのプラズマダメージが大きくなつたためと思われる。

【0046】(実施例2)本実施例では、図3に示した長尺ロール状の導電性基板31を連続搬送できるロール・ツー・ロール(Roll to Roll)形式のイオンビームスペッタ装置を用いて、下記手順(1)～(6)に従って、11種の光起電力素子(太陽電池として機能する素子)を作製した。

【0047】透明導電膜42は、下記作製手順に従って薄膜半導体層41の上に設けた。

(1) 基板送り出しロール341に巻きつけられた実施例1と同様にトリプルセルを設けた導電性基板31を基板送り出し室34に装着し、図3の様にロール342、ロール332を介して基板巻き取りロール331に巻きつけた。

(2) 導電性基板31は、堆積室35等のアース電位に対して電気的に絶縁するために、導電性基板31と接触する各ロール341、342、331および332の表面には、両面テープで絶縁性ポリイミドフィルムを貼った。

(3) 導電性基板31と堆積室35との間の電気抵抗50をテスターで測定したところ、抵抗値はMΩ台を示し、

確かに基板31が電気的にアースに対して絶縁されていることを確認した。

(4) 真空ポンプ(図示せず)で真空中度が 10^{-6} Torr台になるまで、イオンビーム発生室(図示せず)を排気した後、該室にアルゴンガスを導入し、 3×10^{-4} Torrとした。また、酸素(O_2)分圧が 1×10^{-5} Torrとなるように、酸素ガスを導入した。

(5) ヒータ14は、熱電対15の指示値が200°Cになるように出力制御した。ヒータ14による発熱から1時間後に、導電性基板31の搬送を開始した。この時の基板搬送速度は、毎分50cmとした。

(6) 導電性基板31と堆積室35との間に、電圧印加手段として設けた直流電源36により、導電性基板31とアース電位に対して、-120ボルト～+20ボルトの範囲で、下記11ポイントの電圧値を選択し、各電圧値毎の成膜をおこなった。

【0048】上記11ポイントの電圧値として、+20ボルト、+5ボルト、0ボルト(アース)、-5ボルト、-20ボルト、-40ボルト、-60ボルト、-80ボルト、-100ボルト、-110ボルト及び-120ボルトが選択された。成膜圧力は実施例1と同様にした。

【0049】こうして作成した11種の光起電力素子の200luxの蛍光灯下での開放電圧の測定結果を図7に示す。更に、透明導電膜42の上に、銀ペーストをスクリーン印刷して集電電極を形成し、AM1.5(100mW/cm²)の光照射下にて得られた光電変換効率を図8に示す。

【0050】図7及び図8から判るように、電圧が0(アース)ボルト～+10ボルトの場合では、太陽電池としての機能が著しく低下していた。この原因是、薄膜半導体層41表面に発生する電荷が薄膜半導体層41から導電性基板31側に向かって流れる際に、薄膜半導体層41の電気的に弱い部分に集中して流れ、その部分に破壊(ショート)を引き起こすため、と思われる。

【0051】また、セルフバイアス電圧がマイナス側に大きくなり過ぎると(-100ボルトを越えて、よりマイナス側に大きくなる場合)、光起電力素子の機能は低下する。特に、低照度での開放電圧の低下が著しい。この原因は、飛来してくるイオンによる半導体層41へのプラズマダメージが大きくなつたためと思われる。

【0052】(実施例3)本実施例は、図3に図示した装置を用いて実施したものである。

【0053】前記実施例2で用いた導電性基板31への電圧印加を省略し、該導電性基板31をハイ・インピーダンスに設定した他は、実施例2と同様の方法によって薄膜半導体層41の上に透明導電膜42を成膜させた。

【0054】なお、実施例2の手順(5)における熱電対15の指示値が180°Cに設定されるようにヒータ14を加熱制御した他は、実施例2の手順(1)～(5)と

同一の手順を用いた。また、本実施例で用いたイオンビーム発生装置では、高真空室を 10^{-6} Torr台まで排気し、アルゴンガスは、真空中度が0.2mTorrに設定される様に、ガス導入管から導入させた。

【0055】また、透明導電膜堆積中に於いて、導電性基板31と堆積室35との間の電圧を電圧計によって測定したところ、セルフバイアス値が指示値 $V_{self} = -15$ ボルトである-15ボルトの値をほぼ維持していることを確認した。

10 【0056】こうして作成した光起電力素子を20mおきに30cm巾で切り出し、200luxの蛍光灯下で開放電圧を測定した所、0.46ボルト±0.03ボルトと良好な値を示した。更に、薄膜半導体層41の上に銀ペーストをスクリーン印刷して集電電極を形成し、AM1.5(100mW/cm²)の光照射下にて特性評価を行ったところ、光電変換効率で7.3±0.2%と優れた変換効率が得られた。

【0057】(比較例1)前記実施例2で用いた装置に於いて、導電性基板31をアースに接続した他は、実施例2と同様の装置及び成膜方法を用いた。

【0058】こうして作成した光起電力素子は、実施例2と同様の方法によって、光電変換効率を測定したところ、最高でも2.0%であった。この比較用素子の集電電極を陽極にし、導電性基板31を負極にして、両電極間に直流電流を20mA流した時の光起電力素子表面をIRカメラで観察してみると、素子全面に電流のパスができるのが確認できた。この原因は、透明導電膜42を薄膜半導体層41の上に形成する際、導電性基板31がアースされた堆積室35と電気的に接続されているため、薄膜半導体層41表面に発生する電荷が薄膜半導体層41から導電性基板31の側に向かって流れ、この時、薄膜半導体層41の電気的に弱い部分に集中して流れ、その部分に破壊(ショート)が引き起こされたため、と考えられる。

30 【0059】(実施例4)前記実施例3の手順(4)を下記手順(4a)に変更し、更に手順(5)における基板搬送速度を毎分50cmを毎分70cmに変更した他は、実施例3と同様の装置及び方法を用いた。

【0060】手順(4a)イオンビーム発生装置の高真空室の真空中度が 10^{-6} Torr台になるまで排気した後、アルゴンガスを導入し、真空中度を 1.5×10^{-5} Torrにした。

【0061】本実施例における透明導電膜堆積中に於いて、導電性基板31と堆積室35との間の電圧を電圧計によって測定したところ、セルフバイアスの指示値 V_{self} は、-110ボルトであった。

【0062】こうして作成した光起電力素子を実施例3と同様の方法によって測定したところ、80%のサンプルについて、その開放電圧は、0.05ボルト以下と低いものであった。更に、銀ペーストをスクリーン印刷して集

電電極を形成し、AM1.5 (100mW/cm^2) の光照射下にて特性評価を行ったところ、前述80%のサンプルにおいて、その光電変換効率は、最高でも3.5 %であった。

【0063】この比較用素子に設けた集電電極を陽極にし、導電性基板31を負極にして、両電極間に直流電流を20mA流した時の素子表面をIRカメラで観察してみると、素子表面のところどころに直径約30mm前後のボール状の電流のパスができているのが確認できた。これは透明導電膜42を形成する際のイオンビームによりイオン化されたITOイオンによる半導体層41へのプラズマダメージにより何らかの破壊(ショート)が引き起こされたため、と考えられる。

【0064】本発明を適用し得る薄膜半導体層としては、上述の図4に記載の太陽電池用半導体層の他に、アクティブマトリクス駆動によって動作駆動される液晶パネルに使用する薄膜トランジスタ用薄膜半導体層、米国特許第5,184,018公報、米国特許第5,262,649号公報等に記載のセンサー用薄膜半導体層を挙げることができる。

【0065】

【発明の効果】本発明によれば、上記特徴を有するイオンビームスパッタ装置及び半導体装置の製造法を用いて、すなわち該導電性基板を電気的に、ハイ・インピーダンス又はセルフバイアスと同電位に接続することで、非アースに接続させ、導電性基板上に形成された半導体層上に透明導電膜を形成することにより、導電性基板から表面の半導体層に向かって直流電流が流れにくくなり、半導体層の破壊(ショート)を防止できる。また、導電性基板のアースに対する電位は、-100ボルト以上0ボルト未満となるようにスパッタ条件を選んでやることによって、イオンによる半導体層へのプラズマダメージを軽減することができる。

【0066】また、本発明によれば、導電性基板の電位をアースに対して-100ボルト以上0ボルト未満に制御することにより、上記のような半導体層への悪影響をなくすことができるのみでなく、粒径の大きさがそろった密な膜が得られ、低抵抗で、透過率が高く、耐酸性・耐アルカリ性に優れ、かつ、耐熱性に優れた長期使用に対して安定な透明導電膜を形成することができる。

【0067】更に、本発明によれば、グロー放電によるDCマグнетロンスパッタ法に比べてスパッタ室が高真空になるため、グロー放電装置で発生する放電ガスのスパッタ膜への吸収がなくなり、高純度の薄膜、すなわち、

低抵抗で、高透過率の透明導電膜が得られる。

【図面の簡単な説明】

【図1】本発明のイオンビームスパッタ装置の概略構成図である。

【図2】本発明の別のイオンビームスパッタ装置の概略構成図である。

【図3】本発明の別のイオンビームスパッタ装置の概略構成図である。

【図4】本発明で用いた半導体装置の断面図である。

【図5】実施例1によって測定された特性図である。

【図6】実施例1によって測定された特性図である。

【図7】実施例2によって測定された特性図である。

【図8】実施例2によって測定された特性図である。

【符号の説明】

1 1 イオンビーム発生装置

1 1 1 ガス導入管

1 1 2 イオン化ヒータ手段

1 1 3 ビーム加速手段

1 1 4 高真空室

2 0 1 2, 3 5 堆積室

1 2 1 イオンビーム

1 2 2 ターゲット

1 2 3 ターゲット成分

1 2 4 導電性基板

1 2 5 基板加熱用ヒータ

1 2 6 真空室

1 2 7 热電対

1 3 スイッチ

2 1 導電性基板への電圧印加手段

3 0 3 1 ロール状導電性基板

3 2 導電性基板の移動方向を示す矢標

3 3 基板搬入室

3 3 1 卷き取りロール

3 3 2, 3 4 2 送りロール

3 4 基板搬出室

3 4 1 送り出しロール

3 5 2 ターゲット成分

4 1 薄膜半導体層

4 1 1, 4 1 4, 4 1 7 p型半導体層

4 1 2, 4 1 5, 4 1 8 i型半導体層

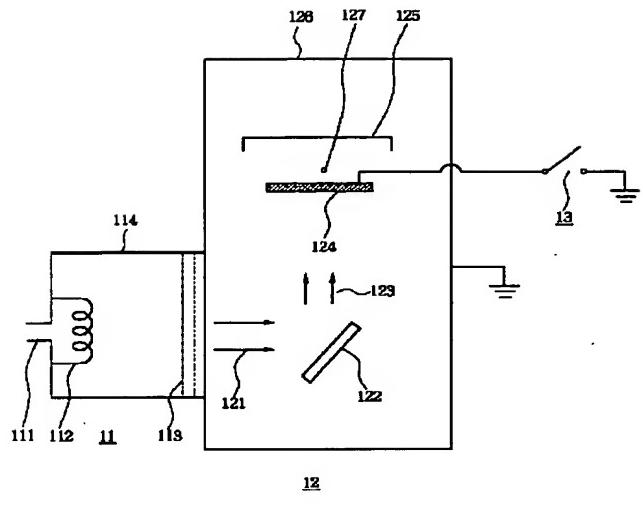
4 1 3, 4 1 6, 4 1 9 n型半導体層

4 2 透明導電膜

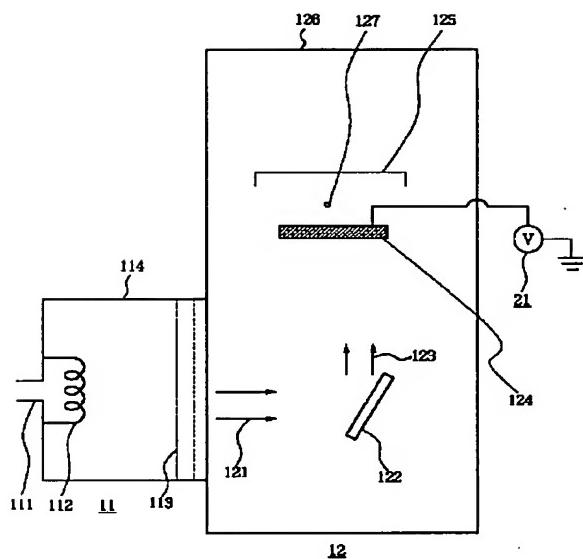
4 3 反射層

4 4 下地透明導電膜

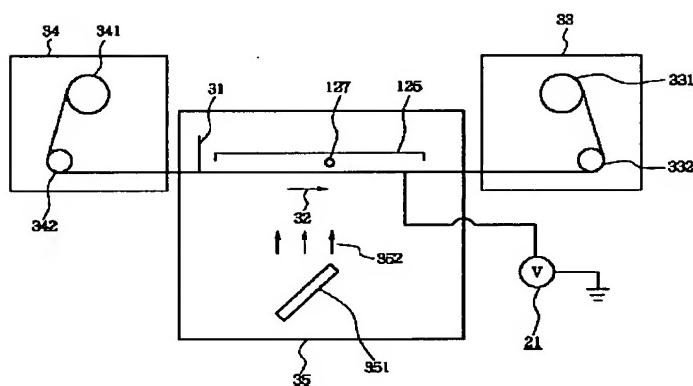
【図1】



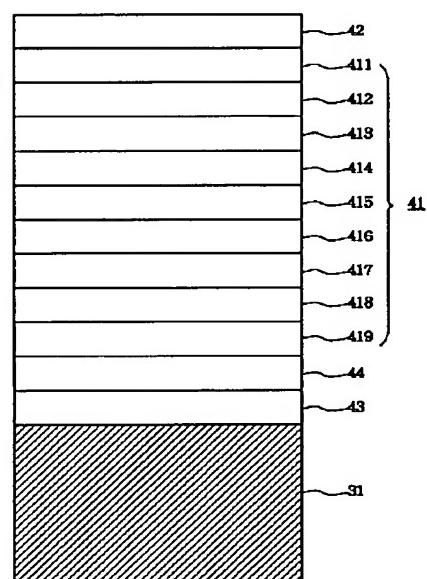
【図2】



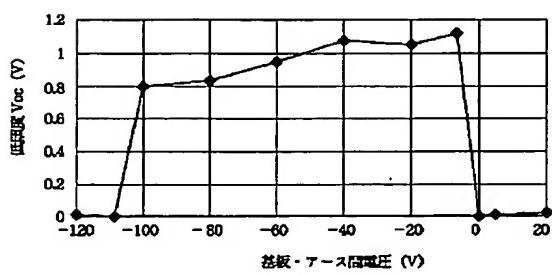
【図3】



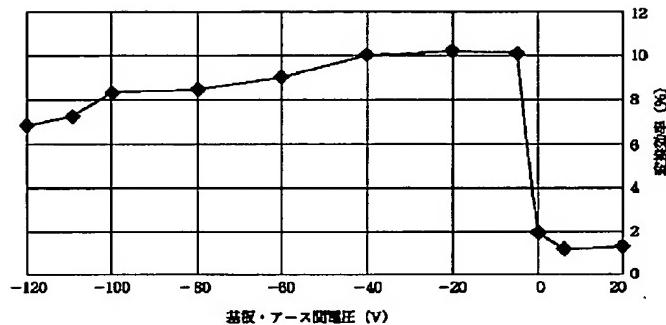
【図4】



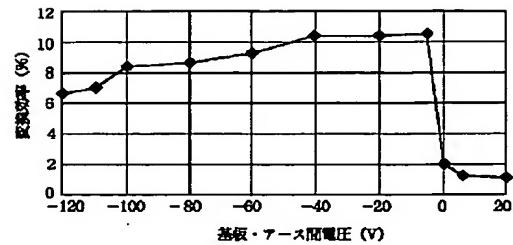
【図5】



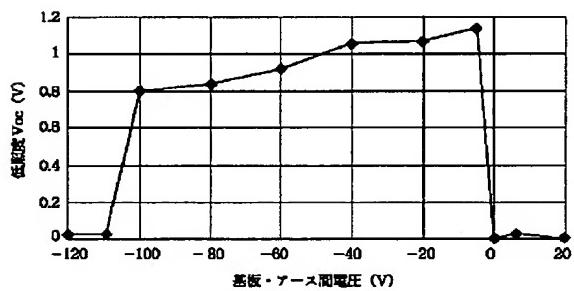
【図6】



【図8】



【図7】



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method of photo-electric-conversion equipment
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H01L 21/203 S
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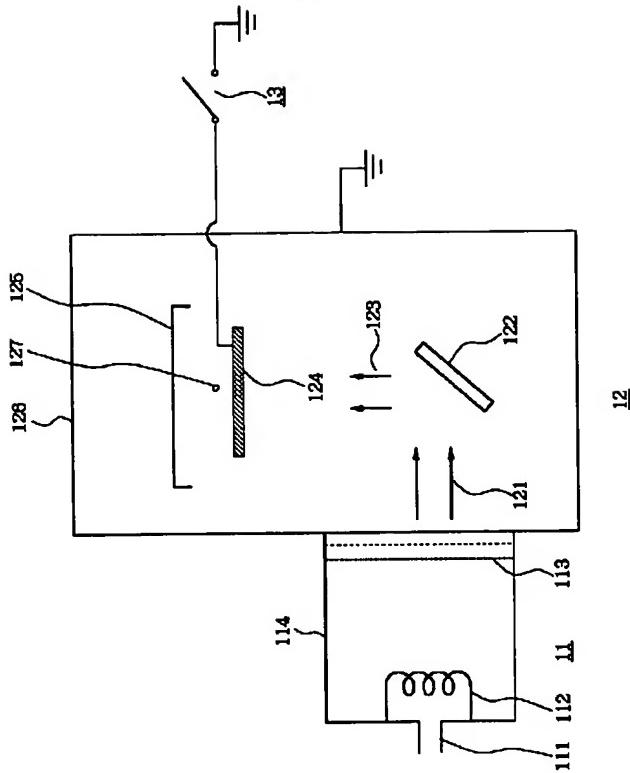
Epitome

(57) [Abstract]

[Technical problem] The bad influence which a semi-conductor layer receives by the ion beam spatter is prevented, and the outstanding semiconductor device is manufactured.

[Means for Solution] a. The exposure of 1st means to generate an ion beam and to turn this ion beam in the predetermined direction, and the ion beam turned in the b. aforementioned predetermined direction 2nd means to hold this target in the location which receives the exposure of this ion beam so that the spatter of this target may be carried out, c. 3rd means to hold the conductive substrate which prepared the semiconductor thin film layer for making said target component by which the spatter was carried out deposit, d. The manufacturing method of the semiconductor device using the ion beam spatter equipment which has 4th means to set the potential of said conductive substrate as non-grounding potential, and this equipment, and a list are provided with the manufacturing method of photo-electric-conversion equipment.

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CLAIMS

[Claim(s)]

[Claim 1] a. So that an ion beam may be generated and the spatter of the target may be carried out by the exposure of 1st means to turn this ion beam in the predetermined direction, and the ion beam turned in the b. aforementioned predetermined direction 2nd means to hold this target in the location which receives the exposure of this ion beam, c. Ion beam

spatter equipment which has 3rd means to hold the conductive substrate which prepared the semi-conductor thin film layer for making said target component by which the spatter was carried out deposit, and 4th means to set the potential of the d. aforementioned conductivity substrate as non-grounding potential.

[Claim 2] Said conductive substrate is ion beam spatter equipment according to claim 1 which is a long picture-like conductivity substrate.

[Claim 3] Said 4th means is ion beam spatter equipment according to claim 1 which has a means to insulate said conductive substrate and ground.

[Claim 4] Said 4th means is ion beam spatter equipment according to claim 1 which has a means to impress an electrical potential difference to this conductive substrate so that it may be set as the polarity as the potential to the ground of said thin film semiconductor layer front face with the same potential to the ground of said conductive substrate.

[Claim 5] Said electrical potential difference is ion beam spatter equipment according to claim 4 set as -100 volts or more less than 0 volt.

[Claim 6] Said thin film semiconductor layer is ion beam spatter equipment according to claim 1 which is a semi-conductor layer with semi-conductor junction.

[Claim 7] Said thin film semiconductor layer is ion beam spatter equipment according to claim 1 which is a semi-conductor layer with the semi-conductor junction formed with non-single crystal silicon.

[Claim 8] Said thin film semiconductor layer is ion beam spatter equipment according to claim 1 which is a semi-conductor layer with the pin junction formed with an amorphous silicon, microcrystal silicon, or polycrystalline silicon, nip junction, pn junction, or np junction.

[Claim 9] a. The process which arranges a target in the location where the ion beam in ion beam spatter equipment is irradiated, b. in the location which the target component generated from said target in said ion beam spatter equipment deposits By generating the process and c. ion beam which arrange the conductive substrate which prepared the thin film semiconductor layer, and turning this ion beam in the predetermined direction Irradiate this ion beam and the spatter of this target is carried out to said target. So that said conductive substrate may become non-grounding potential during the period which is the manufacturing method of the semiconductor device which has the process which makes said target component deposit on said thin film semiconductor layer, and said target component deposits at least The manufacturing method of the semiconductor device characterized by setting up the potential of said

conductive substrate.

[Claim 10] Said conductive substrate is the manufacturing method of the semiconductor device according to claim 9 which is a long picture-like conductivity substrate.

[Claim 11] The manufacturing method of the semiconductor device according to claim 9 which sets up the potential of said conductive substrate by insulating said conductive substrate and ground.

[Claim 12] The manufacturing method of the semiconductor device according to claim 9 which impresses an electrical potential difference to this conductive substrate so that it may be set as the polarity as the potential to the ground of said thin film semiconductor layer front face with the same potential to the ground of said conductive substrate.

[Claim 13] Said electrical potential difference is the manufacturing method of the semiconductor device according to claim 12 set as -100 volts or more less than 0 volt.

[Claim 14] Said thin film semiconductor layer is the manufacturing method of the semiconductor device according to claim 9 which is a semi-conductor layer with semi-conductor junction.

[Claim 15] Said thin film semiconductor layer is the manufacturing method of the semiconductor device according to claim 9 which is a semi-conductor layer with the semi-conductor junction formed with non-single crystal silicon.

[Claim 16] Said thin film semiconductor layer is the manufacturing method of the semiconductor device according to claim 9 which is a semi-conductor layer with the pin junction formed with an amorphous silicon, microcrystal silicon, or polycrystalline silicon, nip junction, pn junction, or np junction.

[Claim 17] The manufacturing method of the semiconductor device according to claim 9 which forms the transparency electric conduction film by deposition of said target component.

[Claim 18] a. The process which arranges a target in the location where the ion beam in ion beam spatter equipment is irradiated, b. The process which arranges the conductive substrate which prepared the thin film semiconductor layer in the location which the target component generated from said target in said ion beam spatter equipment deposits, c. by generating an ion beam and turning this ion beam in the predetermined direction Irradiate this ion beam and the spatter of this target is carried out to said target. So that said conductive substrate may become non-grounding potential during the period which is the manufacturing method of the semiconductor device which has the process which makes said target component deposit on said thin film semiconductor layer, and

said target component deposits at least The manufacturing method of the photo-electric-conversion equipment characterized by setting up the potential of said conductive substrate.

[Claim 19] Said conductive substrate is the manufacturing method of the photo-electric-conversion equipment according to claim 18 which is a long picture-like conductivity substrate.

[Claim 20] The manufacturing method of the photo-electric-conversion equipment according to claim 18 which sets up the potential of said conductive substrate by insulating said conductive substrate and ground.

[Claim 21] The manufacturing method of the photo-electric-conversion equipment according to claim 18 which impresses an electrical potential difference to this conductive substrate so that it may be set as the polarity as the potential to the ground of said thin film semiconductor layer front face with the same potential to the ground of said conductive substrate.

[Claim 22] Said electrical potential difference is the manufacturing method of the photo-electric-conversion equipment according to claim 21 set as -100 volts or more less than 0 volt.

[Claim 23] Said thin film semiconductor layer is the manufacturing method of the photo-electric-conversion equipment according to claim 18 which is a semi-conductor layer with semi-conductor junction.

[Claim 24] Said thin film semiconductor layer is the manufacturing method of the photo-electric-conversion equipment according to claim 18 which is a semi-conductor layer with the semi-conductor junction formed with non-single crystal silicon.

[Claim 25] Said thin film semiconductor layer is the manufacturing method of the photo-electric-conversion equipment according to claim 18 which is a semi-conductor layer with the pin junction formed with an amorphous silicon, microcrystal silicon, or polycrystalline silicon, nip junction, pn junction, or np junction.

[Claim 26] The manufacturing method of the photo-electric-conversion equipment according to claim 18 which forms the transparency electric conduction film by deposition of said target component.

[Translation done.]

* NOTICES *

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacturing method of a semiconductor device and photo-electric-conversion equipment at the ion beam spatter equipment with which it has been improved for forming the electric conduction film on a thin film semiconductor layer with semi-conductor junctional zones made to form with non-single crystal silicon, such as photo-electric-conversion equipments, such as a solar battery, the Rhine photosensor, or an area photosensor, or a thin film semiconductor layer which constitutes a thin film transistor especially an amorphous silicon, microcrystal silicon, or polycrystalline silicon, such as a pin junction layer, and a nip junctional zone, a pn junction layer, and a list.

[0002]

[Description of the Prior Art] After a thin film semiconductor prepares a thin film semiconductor layer on the substrate which prepared the electric conduction film, on this thin film semiconductor layer, it forms the electric conduction film and is component-ized. For example, photo-electric-conversion equipments, such as an above-mentioned photovoltaic cell, prepare a thin film semiconductor layer which was mentioned above on the substrate with a conductive front face, and the transparency electric conduction film is further formed on this thin film semiconductor layer.

[0003] Conventionally, electric conduction film, such as transparency electric conduction film, was formed on the thin film semiconductor layer by vacuum deposition or the DC magnetron sputtering method.

[0004] For example, as an ingredient of this transparency electric conduction film used in the photovoltaic cell by which a semi-conductor layer is formed through a reflecting layer on a conductive substrate, and the transparency electric conduction film is further formed on it, In 203, SnO₂, ZnO, ITO (indium stannic acid ghost), etc. are usually known, and there are a vacuum deposition method, a spatter, a CVD method, a spray method, etc. as the formation approach. Also in this, especially

the ITO transparency electric conduction film is excellent in that transmission, conductivity, and an etching property, and is used best. As the formation approach of this ITO film, the DC magnetron sputtering method is widely used from a predominance from the field of the property of the formed film, and a predominance in the field of productivity.

[0005] In order for the above-mentioned photovoltaic cell to generate electromotive force efficiently, the transparency electric conduction film with more high permeability is required more by low resistance. However, it is extent 10A of rates of sedimentation, and more than sec. that was excellent in mass-production nature by making substrate temperature at the time of membrane formation into comparatively low 230-degree-C or less extent, for example. When the 500A - about 1000A transparency electric conduction film which is the thickness for which it was suitable as transparency electric conduction film on a conductive substrate / reflecting layer / semi-conductor layer is formed, only the transparency electric conduction film whose sheet resistance is at most 50ohms / ** extent is obtained.

[0006] Moreover, the membrane formation approach of the transparency electric conduction film by the ion beam spatter indicated by the publication-number No. 331413 [seven to] official report is proposed. According to the publication of an above-mentioned open specification, special compound semiconductors, such as the gay junction CuInSe₂, are used as a semi-conductor layer. However, in applying this approach to the electric conduction film formation on the thin film semiconductor layer which has amorphous nip junction, for example, it became clear by experiment of this invention person that the following technical problems occur.

[0007] According to the experiment of this invention person, on the thin film semiconductor layer on the conductive substrate in which a photovoltaic cell is made to form namely, by the ion beam spatter When electric conduction film, such as transparency electric conduction film, is formed, it goes to the front face of this thin film semiconductor layer from this conductive substrate, and it is a direct current (this current). what is depended on the flow of the negative charge from the front face of a thin film semiconductor layer to a conductive substrate is presumed -- having -- it flowed, consequently electrically [this thin film semiconductor layer], the current concentrated, it flowed into the weak part (a perimeter -- comparing -- low -- a part [****]), and causing [in that part]-destruction (short) ** became clear. For this reason, the function as a photovoltaic cell fell and was worsening the stability with the passage of time in further prolonged use.

[0008] According to this invention person's knowledge based on the experiment mentioned above, it became clear that the above-mentioned short cause was as follows. Namely, after using roll-like stainless steel and preparing a thin film semiconductor layer in the shape of a roll on this as a conductive substrate especially When the transparency electric conduction film is formed by the ion beam spatter on this thin film semiconductor layer, Since the support roll for stabilizing the supporter for supporting roll-like stainless steel and conveyance etc. is constituted by conductive members, such as a metal, Roll-like stainless steel will be grounded as a result by contact between these. For this reason, at the time of an ion beam spatter, electric field arise between the potential by the side of a thin film semiconductor layer front face, and the ground potential of a conductive substrate. flowing intensively toward a semi-conductor layer front face through the low resistance part where this electric field are impressed to a thin film semiconductor layer, and the current exists in this thin film semiconductor layer from a conductive substrate -- it came out.

[0009] An ion beam spatter has the strong energy of the plasma as compared with DC magnetron sputtering etc. Therefore, the depression of the photovoltaic cell by the above-mentioned current poses a bigger problem. The plasma damage furthermore given to a semi-conductor layer also poses a problem.

[0010]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to provide the improved ion beam spatter equipment which controlled above-mentioned short generating, and a list with the manufacturing method of a semiconductor device and photo-electric-conversion equipment.

[0011] Furthermore, another purpose of this invention is to provide the improved ion beam spatter equipment which mitigated the plasma damage to the semi-conductor layer by the ion at the time of an ion beam spatter, and made it possible to carry out continuation conveyance of the conductive roll-like substrate suitable for mass production method, and a list with the manufacturing method of a semiconductor device and photo-electric-conversion equipment.

[0012] Moreover, the magnitude of particle size is uniform, distribution of a particle is dense, and it is low resistance, and another purpose of this invention is high permeability, it is excellent in acid resistance and alkali resistance, and is excellent in thermal resistance, and is to offer the manufacturing method of the semiconductor device which prepared this transparency electric conduction film in the ion beam spatter equipment list which made it possible to form the stable

transparence electric conduction film to long-term use, and photo-electric-conversion equipment.

[0013]

[Means for Solving the Problem] This invention so that a. ion beam may be generated and the spatter of the target may be carried out by the exposure of 1st means to turn this ion beam in the predetermined direction, and the ion beam turned in the b. aforementioned predetermined direction 2nd means to hold this target in the location which receives the exposure of this ion beam, c. The ion beam spatter equipment which has 3rd means to hold the conductive substrate which prepared the semi-conductor thin film layer for making said target component by which the spatter was carried out deposit, and 4th means to set the potential of the d. aforementioned conductivity substrate as non-grounding potential is offered.

[0014] Moreover, the process to which this invention arranges a target in the location where the ion beam in a. ion beam spatter equipment is irradiated, b. in the location which the target component generated from said target in said ion beam spatter equipment deposits By generating the process and c. ion beam which arrange the conductive substrate which prepared the thin film semiconductor layer, and turning this ion beam in the predetermined direction Irradiate this ion beam and the spatter of this target is carried out to said target. So that it may have the process which makes said target component deposit on said thin film semiconductor layer and said conductive substrate may become non-grounding potential during the period which said target component deposits at least The manufacturing method of the semiconductor device characterized by setting up the potential of said conductive substrate and the manufacturing method of photo-electric-conversion equipment are offered.

[0015]

[Embodiment of the Invention]

(Equipment which carries out ion beam spatter formation of the transparence electric conduction film) Drawing 1 is the outline block diagram showing an example of the ion beam spatter equipment which carries out ion beam spatter formation of the transparence electric conduction film concerning this invention.

[0016] In drawing 1 , the equipment of this invention accelerates the argon gas installation tubing 111, the ionization heater 112 which excites the introduced argon gas to ion, and generating ion in the shape of a beam. It is arranged in the ion beam generator 11 equipped with the accelerator 113 made to carry out outgoing radiation in the

predetermined direction in the vacuum chamber 114, and the location which receives the exposure of the ion beam 121 of said predetermined direction. In order to make the target 122 in which a spatter is carried out by the exposure of this ion beam 121, and said target component 123 by which the spatter was carried out deposit The heater 125 for substrate heating which heats the conductive substrate 124 which formed the thin film semiconductor layer 41 of lower ** illustrated to arranged drawing 4 , and this conductive substrate 124, and the thermocouple 127 for temperature control in the deposition room 12 and list which it had in the vacuum chamber 126 during the deposition period of said target component 123 In order to insulate said conductive substrate 124 electrically to a ground, it is ion beam spatter equipment which has SUWITCHI 13 set as opening. Opening of this SUWITCHI 13 insulates between said conductive substrates 124 and ground potentials, and membrane formation of the transparency electric conduction film 42 illustrated on the thin film semiconductor layer 41 at drawing 4 of lower ** is carried out.

[0017] Drawing 2 is illustrating another mode of this invention equipment. The equipment illustrated to drawing 2 accelerates the argon gas installation tubing 111, the ionization heater 112 which makes ion excite the argon gas made to introduce, and generating ion in the shape of a beam. It arranges in the ion beam generator 11 equipped with the accelerator 113 made to carry out outgoing radiation in the predetermined direction in the vacuum chamber 114, and the location which receives the exposure of the ion beam 121 of said predetermined direction. In order to make the target 122 in which a spatter is carried out by the exposure of this ion beam 121, and said target component 123 by which the spatter was carried out deposit The heater 125 for substrate heating which heats the conductive substrate 124 which formed the thin film semiconductor layer 41 illustrated to arranged drawing 4 , and this conductive substrate 124, and the thermocouple 127 for temperature control in the deposition room 12 and list which it had in the vacuum chamber 126 during the deposition period of said target component 123 It is ion beam spatter equipment which has an electrical-potential-difference impression means 21 to set said conductive substrate 124 as the -100-volt or more range of less than 0 volt to a ground.

[0018] Moreover, by another example of this invention, it can fix to the substrate electrode holder of the insulating insulator which was able to be done with the non-illustrated alumina, and, thereby, the conductive substrate 124 can insulate the conductive substrate 124 electrically to

the ground potential of vacuum chamber 126 grade.

[0019] the potential condition of said thin film semiconductor layer 41 front face of the electrical-potential-difference impression means 21 in drawing 2 is minus potential to a ground during an ion beam sputter period -- being based -- said conductive substrate 124 -- a ground -- receiving -- the -100-volt or more range of less than 0 volt -- desirable -- the -60-volt or more range of less than 0 volt -40-volt or more the electrical potential difference of the range of less than 0 volt can be impressed especially preferably. Consequently, the transparence electric conduction film 42 illustrated on the thin film semiconductor layer 41 at drawing 4 of lower ** is formed.

[0020] Moreover, when the electrical potential difference impressed to said conductive substrate 124 by said electrical-potential-difference impression means 21 became large at the minus side exceeding -100 volts according to the experiment of this invention person, it became clear that the plasma damage to semi-conductor layer 41 front face occurred.

[0021] Drawing 3 illustrates another mode of this invention. In drawing 3 , the roll-like conductivity substrate 31 currently fabricated with metal roll objects, such as roll-like stainless steel, is conveyed continuously or in step along the direction of **** 32. The bearing in the substrate carrying-in room 33 set as the vacua (not shown) is fixed, and the point of this roll-like conductivity substrate 31 is rolled round by the rolling-up roll 331. On the other hand, the bearing (not shown) of the substrate taking-out room 34 set as the vacua is fixed, and the back end section of the roll-like conductivity substrate 31 is beforehand wound around the delivery roll 341. The delivery rolls 332 and 342 which the driving source (not shown) which drives each bearing is prepared in the substrate taking-out room 34 and the substrate carrying-in room 33, and make regularity horizontally tension of the roll-like conductivity substrate 31 under migration are formed. It is connected by the non-illustrated gas gate between the deposition room 35 and the substrate carrying-in room 33 and between the deposition room 35 and the substrate taking-out room 34, and a substrate 31 can touch them no longer at atmospheric air.

[0022] As a roll-like conductivity substrate 31 used by this invention, the thin film semiconductor layer 41 of lower ** illustrated to drawing 4 is preferably formed on this roll-like conductivity substrate 31 by using the Rolle Thu Rolle method indicated by the Provisional-Publication-No. No. 43413 [57 to] official report, the publication-number No. 299823 [four to] official report, etc., and its equipment.

[0023] The Rolle Thu Rolle method used by this invention, and its

equipment By passing two or more membrane formation rooms which made this roll-like conductivity substrate become independent with nonproliferation junction means, such as a gas gate means, during continuation conveyance of a roll-like conductivity substrate They are the approach of forming continuously a thin film semiconductor layer with semi-conductor junctional zones made to form with non-single crystal silicon, such as an amorphous silicon, microcrystal silicon, or polycrystalline silicon, such as a pin junction layer, and a nip junctional zone, a pn junction layer, on a roll-like conductivity substrate, and its equipment.

[0024] Membrane formation of the transparency electric conduction film 42 is carried out at the thin film semiconductor layer 41 top in the deposition room 35 of the ion beam spatter equipment with which the roll-like conductivity substrate 31 with which this thin film semiconductor layer 41 is formed consists of an ion beam generator (not shown) and a deposition room 35. What was used in the example illustrated to above-mentioned drawing 1 and 2, and the same thing can be used for an ion beam generator and the deposition room 35.

[0025] In the equipment illustrated to drawing 3 , in order to insulate said conductive substrate 31 electrically to a ground during the deposition period of the target component 352 produced by the spatter of a target 351, by this example, the insulating polyimide film (not shown) is beforehand stuck on the front face of each rolls 341, 342, 331, and 332 in contact with the conductive substrate 31 with the double-sided tape. Thereby, the conductive substrate 31 was insulated to the potential of the ion beam spatter equipment 35 grade connected to the ground. As an electric insulation means, the insulating material which consists of resin, such as Teflon, paper, etc. may be stuck on the front face of each rolls 341, 342, 331, and 332 besides a ****. Moreover, insulating materials, such as paint, may be applied to the front face of each rolls 341, 342, 331, and 332. Moreover, resin, such as Teflon, may be infiltrated into the front face of each rolls 341, 342, 331, and 332. Furthermore, the thing made of resin, such as Teflon and Dirline, may be used as a bearing (not shown) of the revolving shaft of each rolls 341, 342, 331, and 332. Moreover, some of these means may be combined.

[0026] Moreover, in the equipment illustrated to drawing 3 , said conductive substrate 31 is connectable with non-grounding potential during the deposition period of the target component 352. The applied voltage to the conductive substrate 31 by the electrical-potential-difference impression means 21 in this case is good to set it as the -100-volt or more range of less than 0 volt of the self-bias potential

between the conductive substrate generated at the time of an ion beam spatter, and ground potential, and this potential. The electrical potential difference from this electrical-potential-difference impression means is not limited to direct current voltage, and may superimpose alternating voltage, RF electrical potential difference, etc. on direct current voltage.

[0027] The ion source of hot cathode electron impact can be used for ion beam generating of above-mentioned drawing 1 , drawing 2 , and the ion beam spatter equipment in the example of the illustration to drawing 3 . Into the deposition room 12 or 35, incidence of the generated ion beam is carried out to the target aslant arranged to an ion beam, and it carries out the spatter of the target. As a target, the pellet (for In 203, 90wt%-Sn02 is a 10wt(s)% mixed sintered compact) of ITO can be used. The relative density of a pellet has [that what is necessary is just 65% or more] 80% or more of still more preferably good thing 70% or more preferably.

[0028] As an ingredient of the above-mentioned target, Sn02, In203, Zn0, etc. may be used in addition to ITO. Moreover, instead of the target using an oxide which was mentioned above, the metal pellet of InSn or Zn can be used and a transparent conductive oxide film can be formed by this, using oxygen as reactant gas.

[0029] Moreover, the conductive substrate 124, 31 and the deposition room 12, or the electrical potential difference between 35 is the above-mentioned self-bias during the period which has deposited the transparency electric conduction film 42. It is measured by the voltmeter as Vself. it is set to a self-bias electrical potential difference (V_{self}) and $-100 \text{ V} \leq V_{self} < 0 \text{ V}$ -- as -- spatter conditions (an ion beam current (preferably 1A-500A) --) A membrane formation pressure (preferably $3 \times 10^{-5} - 1 \times 10^{-2}$ Torr), oxygen tension (preferably 0 - 5×10^{-4} Torr), It is good to choose the distance between a conductive substrate and a target (preferably 50mm - 800mm), the drawer electrical potential difference (preferably 0.2-30kV) of ion, etc. in order to mitigate more the plasma damage to the semi-conductor layer by ion V_{self} desirable $-60 \text{ V} < V_{self} < 0 \text{ V}$ -- further -- desirable $-40 \text{ V} < V_{self} < 0 \text{ V}$ It is good to choose spatter conditions (an ion beam current, a membrane formation pressure, the distance between a substrate and a target, drawer electrical potential difference of ion, etc.) so that it may become.

[0030] Moreover, as a heater 125 for substrate heating for heating the conductive substrate 124 or 31 during a membrane formation period, a sheath heater, an infrared lamp, etc. can be used, and it controls by the equipment of this invention so that the indicated value of the

thermocouple 127 installed in right above [of the conductive substrates 124 or 31] becomes fixed.

[0031] The thing which carries out annealing processing of the front face of the stainless plate (sus430) of 0.2mm in thickness, and 50mm angle into inert gas as a conductive substrate 31 used by this invention and which carried out BA (bright annealing; bright annealing) processing, Although what carried out BA processing of the front face of a stainless steel roll (sus430) with the thickness of 0.2mm, a width [of 360mm], and a die length of 300m can be used, in this invention, it is not limited to these things. As surface treatment, it is not limited to the above-mentioned BA processing, and the split-face-ized thing (for example, No. 2D steel plate) to depend on having made the concave convex muscle form in a front face by heat treatment and acid-washing processing after cold rolling can be used. Moreover, as a conductive substrate 31, a zinc steel plate, an aluminum plate (roll), the plastic film (tape) that carried out galvanized steel sheet (roll) metallurgy group plating can be used other than the above-mentioned stainless plate (roll).

[0032] The reflecting layer 43 formed by metal membranes, such as aluminum film, a silver film, nickel film, and a copper film, may be formed in the conductive substrate 124 used by this invention, or the front face of 31. On this reflecting layer 43, the transparence electric conduction film 44, such as zinc-oxide film and ITO film, may accumulate. As for these reflecting layers 43 and the substrate transparence electric conduction film 44, it is desirable that membranes are formed by the DC magnetron sputtering method.

[0033] The thin film semiconductor layer 41 on the conductive substrate 124 used by this invention can use a cel with pin junction as plurality, for example, a tandem, or a triple component. For example, the semiconductor layer for photovoltaic cells preferably used in this invention is formed by the plasma-CVD method. namely, -- as ingredient gas SiH₄, PH₃, and H₂ -- using -- power -- supplying -- It is n mold as a n-type-semiconductor layer 419. SiH₄, GeH₄, and H₂ are further used for an a-Si layer. It is i mold as an i-type semiconductor layer 418. In an a-SiGe layer, SiH₄, BF₃, and H₂ are used continuously. The 1st nip cel which carried out sequential formation of the p mold muc(microcrystal)-Si layer as a p type semiconductor layer 417 is prepared. Then, the laminating of the 2nd cel which has the n-type-semiconductor layer 416, the i-type semiconductor layer 415, and the p type semiconductor layer 414 as a cel of a two-layer eye is carried out. Furthermore, the 3rd n-type-semiconductor layer 413, the above-mentioned i mold The laminating

of the 3rd cel with the i-type semiconductor layer 412 and the p type semiconductor layer 411 which are a semi-conductor layer which changed the a-SiGe layer into the i mold a-Si layer is carried out. The semi-conductor layer for triple mold photovoltaic cells which used this 3rd cel as the top cel, and carried out the laminating is mentioned. This thin film semiconductor layer 41 is not restricted to amorphous one, a microcrystal, or polycrystal. Moreover, the count which piles up nip should just be one or more. Furthermore, as a thin film semiconductor layer 41, it may not be limited to the configuration of nip junction, and you may be various zygotes, such as pin junction, and pn junction, np junction.

[0034] (How to carry out ion beam spatter formation of the transparency electric conduction film) How to form the transparency electric conduction film hereafter using the equipment illustrated to drawing 1 is explained according to a production procedure.

[0035] First, it checked that the substrate 124 was electrically insulated to a ground by equipping the substrate electrode holder made from an insulator (not shown) with a substrate 124, and measuring the electric resistance between the conductive substrate 124 and the deposition room 12 with a circuit tester first. Although it is desirable since 800k or more ohms of resistance at this time can lessen the current which flows the more the more it is high, there should just be still more preferably more than 600komega preferably that there should just be 300k or more ohms.

[0036] Next, after decompressing ** 114 to the suitable degree of vacuum with the vacuum pump (not shown) and considering as the high vacuum room 114, argon gas was introduced in this high vacuum room 114. Moreover, the conductive substrate 124 was heated to temperature predetermined at a heater 14 at this time.

[0037] Then, the opening of an argon flow rate and/or an exhaust air bulb having adjusted the drawer electrical potential difference of the ion beam current of an ion gun, and ion etc., and this having adjusted the membrane formation pressure, and maintaining a desired self-bias electrical potential difference according to a power source (not shown), on the front face 41 of a substrate 124, i.e., a thin film semiconductor layer, it formed so that it might become the thickness of a request of the transparency electric conduction film 42.

[0038] (Example 1) The equipment of illustration was used for drawing 2 in this example. On the conductive substrate 124, a plasma-CVD method is used beforehand. Under the present circumstances, n mold amorphous silicon layer (10nm), i mold amorphous silicon germanium layer (200nm),

p mold microcrystal silicon layer (5nm), n mold amorphous silicon layer (10nm), i mold amorphous silicon germanium layer (100nm), The triple cel was prepared by depositing p mold microcrystal silicon layer (5nm), n mold amorphous silicon layer (10nm), i mold amorphous silicon layer (70nm), and p mold microcrystal silicon layer (5nm) in order. The electrical potential difference V_0 of a during [the conductive substrate 124 and a ground] was changed to the electrical potential difference of the 11 following points which is the range of -120 volt $\leq V_0 \leq +20$ volt, the transparence electric conduction film was formed, each transparence electric conduction film was prepared, and 11 sorts of photovoltaic cells (component which functions as a solar battery) were produced according to following procedure (1) - (5).

[0039] As an electrical-potential-difference value of 11 points, +20 volts, +5 volts, 0 volt (ground), -5 volts, -20 volts, -40 volts, -60 volts, -80 volts, -100 volts, -100 volts, and -120 volts were chosen.

[0040] (1) The conductive substrate 124 was fixed to the substrate electrode holder (not shown) of the insulating insulator which was able to be done with the alumina.

(2) When the electric resistance between the conductive substrate 124 and the deposition room 12 was measured with the circuit tester, resistance showed the base of Mohms, and it checked that the substrate 124 was electrically insulated to a ground to be sure.

(3) After exhausting the inside of ** 114 and considering as the high vacuum room 114 until the degree of vacuum became a 10⁻⁶Torr base with the vacuum pump (not shown), argon gas was introduced from the gas installation tubing 111 in this ** 114.

(4) The output control of the heater 125 was carried out so that the indicated value of a thermocouple 15 might become 190 degrees C. In addition, it was made for thickness to become 700 ** in general.

(5) The self-bias electrical potential difference V_{self} between the conductive substrate 124 and the deposition room 12 was set as the table 1 of -120 volt $\leq V_{self} < 0$ volt within the limits as the publication by a power source's (not shown) adjusting the drawer electrical potential difference of the ion beam current of an ion gun, and ion etc., and adjusting a membrane formation pressure by opening accommodation of an argon flow rate and/or an exhaust air bulb as the following table 1. Moreover, floating was short-circuited during membrane formation and membrane formation by $V_{self}=0$ volt was also performed. Furthermore, membrane formation while impressing the applied voltage V_0 to the conductive substrate 124 in 0 volt $\leq V_0 \leq +20$ volt was also performed using DC power supply.

[0041]

[Table 1]

表 1

セルフ・バイアス電圧 (ボルト)	成膜圧力 (Torr)
- 120	1×10^{-6}
- 110	2×10^{-6}
- 100	3×10^{-6}
- 80	5×10^{-6}
- 60	8×10^{-6}
- 40	2×10^{-4}
- 20	5×10^{-4}
- 5,0, + 5, + 20	5×10^{-3}

[0042] In this way, 200lux(es) of the created photovoltaic cell (looks) The measurement result of the open circuit voltage under a fluorescent lamp is shown in drawing 5 .

[0043] Furthermore, a silver paste is screen-stenciled on the front face of the transparency electric conduction film 42 of 11 sorts of solar batteries mentioned above, a current collection electrode is formed in it, and the photoelectric conversion efficiency acquired under the optical exposure of AM1.5 (100 mW/cm²) is shown in drawing 6 .

[0044] In the case where an electrical potential difference is 0 volt (ground) -+10 volt, drawing 5 and drawing 6 show that the function of a photovoltaic cell falls remarkably. It concentrates on a weak part electrically, and flows, and this is considered for [of the semi-conductor layer 41] causing destruction (short) in the part, in case the negative charge generated on semi-conductor layer 41 front face flows toward the conductive substrate 124 side from the semi-conductor layer 41.

[0045] Moreover, if a self-bias electrical potential difference becomes large too much at a minus side, the function of a photovoltaic cell will fall (when becoming large more at a minus side exceeding -100 volts). Especially, the fall of the open circuit voltage in a low illuminance is remarkable. This cause is considered because the plasma damage to the semi-conductor layer 41 by the ion coming flying became large.

[0046] (Example 2) In this example, 11 sorts of photovoltaic cells (component which functions as a solar battery) were produced according to following procedure (1) - (6) using the ion beam spatter equipment of the roll two roll (Roll to Roll) format which can carry out continuation conveyance of the conductive substrate 31 of the shape of a long roll

shown in drawing 3 .

[0047] The transparency electric conduction film 42 was formed on the thin film semiconductor layer 41 according to the following production procedure.

(1) The substrate send room 34 was equipped with the conductive substrate 31 which prepared the triple cel like the example 1 twisted around the substrate delivery roll 341, and it twisted around the substrate rolling-up roll 331 through the roll 342 and the roll 332 like drawing 3 .

(2) The conductive substrate 31 stuck the insulating polyimide film on the front face of each rolls 341, 342, 331, and 332 in contact with the conductive substrate 31 with the double-sided tape, in order to insulate electrically to the ground potential of deposition room 35 grade.

(3) When the electric resistance between the conductive substrate 31 and the deposition room 35 was measured with the circuit tester, resistance showed the base of Mohms and it checked that the substrate 31 was electrically insulated to a ground to be sure.

(4) After exhausting an ion beam generating room (not shown), argon gas was introduced into this ** and it was referred to as 3×10^{-4} Torr, until the degree of vacuum became a 10^{-6} Torr base with the vacuum pump (not shown). Moreover, oxygen gas was introduced so that an oxygen (O₂) partial pressure might serve as 1×10^{-5} Torr.

(5) The output control of the heater 14 was carried out so that the indicated value of a thermocouple 15 might become 200 degrees C. Conveyance of the conductive substrate 31 was started 1 hour after generation of heat at a heater 14. The substrate bearer rate at this time could be per minute 50cm.

(6) To the conductive substrate 31 and ground potential, in -120 volts - +20 volts, the electrical-potential-difference value of the 11 following points was chosen, and every electrical-potential-difference value was formed by DC power supply 36 prepared as an electrical-potential-difference impression means between the conductive substrate 31 and the deposition room 35.

[0048] As an electrical-potential-difference value of the 11 above-mentioned points, +20 volts, +5 volts, 0 volt (ground), -5 volts, -20 volts, -40 volts, -60 volts, -80 volts, -100 volts, -110 volts, and -120 volts were chosen. The membrane formation pressure was made to be the same as that of an example 1.

[0049] In this way, 200lux(es) of 11 sorts of created photovoltaic cells The measurement result of the open circuit voltage under a fluorescent lamp is shown in drawing 7 . Furthermore, on the transparency electric

conduction film 42, a silver paste is screen-stenciled, a current collection electrode is formed, and the photoelectric conversion efficiency acquired under the optical exposure of AM1.5 (100 mW/cm²) is shown in drawing 8 .

[0050] In the case where an electrical potential difference is 0 volt (ground) -+10 volt, the function as a solar battery was falling remarkably so that drawing 7 and drawing 8 might show. In case the charge generated on thin film semiconductor layer 41 front face flows toward the conductive substrate 31 side from the thin film semiconductor layer 41, it concentrates on a weak part electrically and flows, and this cause is considered in order [of the thin film semiconductor layer 41] to cause destruction (short) in that part.

[0051] Moreover, if a self-bias electrical potential difference becomes large too much at a minus side, the function of a photovoltaic cell will fall (when becoming large more at a minus side exceeding -100 volts). Especially, the fall of the open circuit voltage in a low illuminance is remarkable. This cause is considered because the plasma damage to the semi-conductor layer 41 by the ion coming flying became large.

[0052] (Example 3) This example is carried out using the equipment illustrated to drawing 3 .

[0053] Omitted the electrical-potential-difference impression to the conductive substrate 31 used in said example 2, and this conductive substrate 31 was set as the high impedance, and also the transparency electric conduction film 42 was made to form on the thin film semiconductor layer 41 by the same approach as an example 2.

[0054] In addition, heating control of the heater 14 was carried out so that the indicated value of the thermocouple 15 in the procedure (5) of an example 2 might be set as 180 degrees C, and also the same procedure as procedure [of an example 2] (1) - (5) was used. Moreover, the high vacuum room was exhausted to the 10-6Torr base, and argon gas was made to introduce into the appearance by which a degree of vacuum is set as 0.2mTorr(s) from gas installation tubing in the ion beam generator used by this example.

[0055] moreover, the place which measured the electrical potential difference between the conductive substrate 31 and the deposition room 35 with the voltmeter during transparency electric conduction film deposition -- a self-bias value -- indicated value Vself =-15 volt it is -- it checked maintaining the -15 volt value mostly.

[0056] In this way, the created photovoltaic cell is started by 30cm width every 20m, and it is 200lux. Place which measured open circuit voltage under the fluorescent lamp 0.46-volt **0.03 volts and a good

value were shown. Furthermore, when the silver paste was screen-stenciled, the current collection electrode was formed on the thin film semiconductor layer 41 and characterization was performed under the optical exposure of AM1.5 (100mW/cm²), 7.3**0.2% and the outstanding conversion efficiency were acquired with photoelectric conversion efficiency.

[0057] (Example 1 of a comparison) In the equipment used in said example 2, the conductive substrate 31 was connected to the ground, and also the same equipment as an example 2 and the membrane formation approach were used.

[0058] In this way, the highest was also 2.0% when the created photovoltaic cell measured photoelectric conversion efficiency by the same approach as an example 2. The current collection electrode of this component for a comparison was made into the anode plate, and the conductive substrate 31 was used as the negative electrode, and when the photovoltaic-cell front face when passing 20mA of direct current between two electrodes was observed with IR camera, it has checked that the pass of a current was made all over a component. Since this cause is electrically connected with the deposition room 35 where the conductive substrate 31 was grounded in case it forms the transparency electric conduction film 42 on the thin film semiconductor layer 41, At this time, the charge generated on thin film semiconductor layer 41 front face flows toward the conductive substrate 31 side from the thin film semiconductor layer 41, it concentrates on a weak part electrically and flows, and since [of the thin film semiconductor layer 41] destruction (short) was caused in that part, it thinks.

[0059] (Example 4) Changed the procedure (4) of said example 3 into the following procedure (4a), and per minute 50cm was further changed into per minute 70cm for the substrate bearer rate in a procedure (5), and also the same equipment and same approach as an example 3 were used.

[0060] After exhausting until the degree of vacuum of the high vacuum room of a procedure (4a) ion beam generator became a 10⁻⁶Torr base, argon gas was introduced and the degree of vacuum was set to 1.5x10⁻⁵Torr.

[0061] the place which measured the electrical potential difference between the conductive substrate 31 and the deposition room 35 with the voltmeter during the transparency electric conduction film deposition in this example -- the indicated value Vself of self-bias -110 volt it was .

[0062] in this way, the place which measured the created photovoltaic cell by the same approach as an example 3 -- 80% of sample -- the -- Open circuit voltage was as low as 0.05 volts or less. Furthermore, when

the silver paste was screen-stenciled, the current collection electrode was formed and characterization was performed under the optical exposure of AM1.5 (100 mW/cm²), as for the photoelectric conversion efficiency, in the sample of 80% of above-mentioned, the highest was also 3.5 %.

[0063] The current collection electrode prepared in this component for a comparison was made into the anode plate, and the conductive substrate 31 was used as the negative electrode, and when the component front face when passing 20mA of direct current between two electrodes was observed with IR camera, it has checked that the pass of the current of the shape of a ball before and behind the diameter of about 30mm was made into some places on the front face of a component. Since a certain destruction (short) was caused by the plasma damage to the semi-conductor layer 41 by the ITO ion ionized by the ion beam at the time of forming the transparency electric conduction film 42, this is considered. [0064] The thin film semiconductor layer for sensors of a publication can be mentioned to the thin film semiconductor layer for thin film transistors used for the liquid crystal panel in which a drive of operation is carried out as a thin film semiconductor layer which can apply this invention by the active-matrix drive other than the semi-conductor layer for solar batteries given in above-mentioned drawing 4 , the 5,184,018th official report of an United States patent, a U.S. Pat. No. 5,262,649 official report, etc.

[0065]

[Effect of the Invention] According to this invention, electrically this conductive substrate by connecting with a high impedance, or self-bias and this potential, using the manufacturing method of the ion beam spatter equipment which has the above-mentioned description, and a semiconductor device By making it connect with un-grounding and forming the transparency electric conduction film on the semi-conductor layer formed on the conductive substrate, a direct current stops being able to flow easily toward a surface semi-conductor layer from a conductive substrate, and destruction (short) of a semi-conductor layer can be prevented. Moreover, the potential to the ground of a conductive substrate can mitigate the plasma damage to the semi-conductor layer by ion by choosing spatter conditions so that it may become -100 volts or more less than 0 volt.

[0066] Moreover, according to this invention, the stable transparency electric conduction film can be formed to the long-term use which the dense film to which the magnitude of particle size was equal was obtained, and whose permeability was high, and was excellent in acid resistance and alkali resistance with low resistance, and it not only

can lose the bad influence to the above semi-conductor layers, but was excellent in thermal resistance by controlling the potential of a conductive substrate to -100 volts or more less than 0 volt to a ground. [0067] Furthermore, according to this invention, since a spatter room becomes a high vacuum compared with the DC magnetron sputtering method by glow discharge, the occlusion to the spatter film of the discharge gas which occurs with glow discharge equipment is lost, and the transparency electric conduction film of high permeability is obtained with the thin film of a high grade, i.e., low resistance.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the outline block diagram of the ion beam spatter equipment of this invention.

[Drawing 2] It is the outline block diagram of another ion beam spatter equipment of this invention.

[Drawing 3] It is the outline block diagram of another ion beam spatter equipment of this invention.

[Drawing 4] It is the sectional view of the semiconductor device used by this invention.

[Drawing 5] It is the property Fig. measured by the example 1.

[Drawing 6] It is the property Fig. measured by the example 1.

[Drawing 7] It is the property Fig. measured by the example 2.

[Drawing 8] It is the property Fig. measured by the example 2.

[Description of Notations]

11 Ion Beam Generator

111 Gas Installation Tubing

112 Ionization Heater Means

113 Beam Acceleration Means
114 High Vacuum Room
12 35 Deposition room
121 Ion Beam
122 Target
123 Target Component
124 Conductive Substrate
125 Heater for Substrate Heating
126 Vacuum Chamber
127 Thermocouple
13 SUWITCHI
21 Electrical-Potential-Difference Impression Means to Conductive Substrate
31 Roll-like Conductivity Substrate
32 **** Which Shows the Migration Direction of Conductive Substrate
33 Substrate Carrying-in Room
331 Rolling-Up Roll
332 342 Delivery roll
34 Substrate Taking-Out Room
341 Delivery Roll
352 Target Component
41 Thin Film Semiconductor Layer
411, 414, 417 P type semiconductor layer
412, 415, 418 I-type semiconductor layer
413, 416, 419 N-type-semiconductor layer
42 Transparency Electric Conduction Film
43 Reflecting Layer
44 Substrate Transparency Electric Conduction Film

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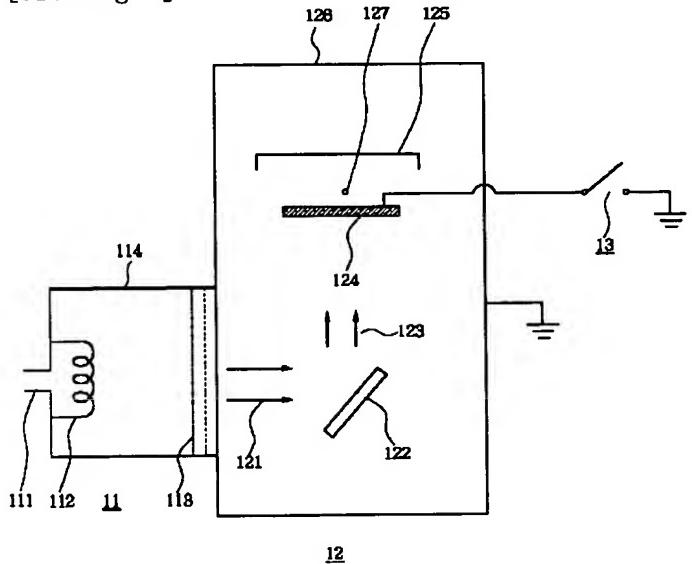
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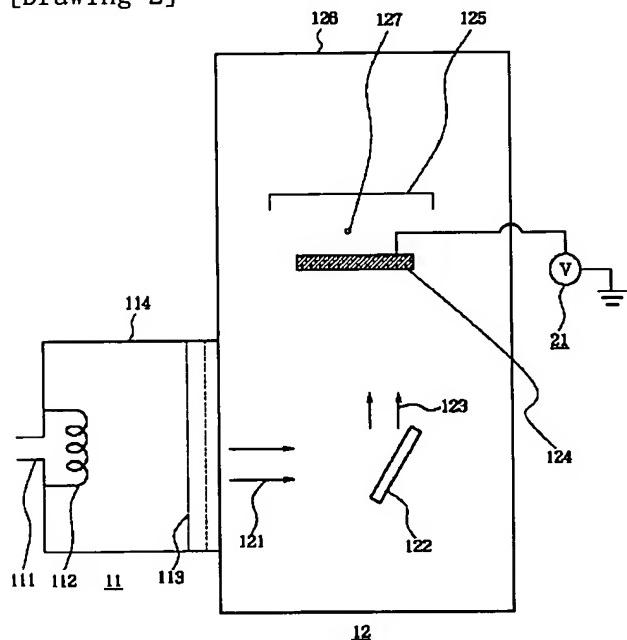
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DRAWINGS

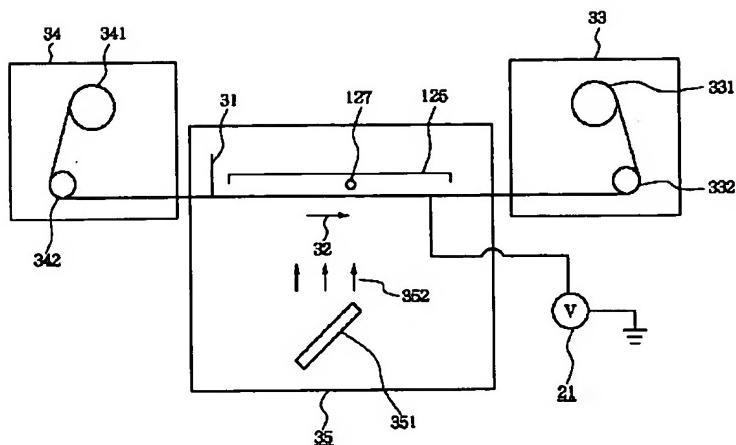
[Drawing 1]



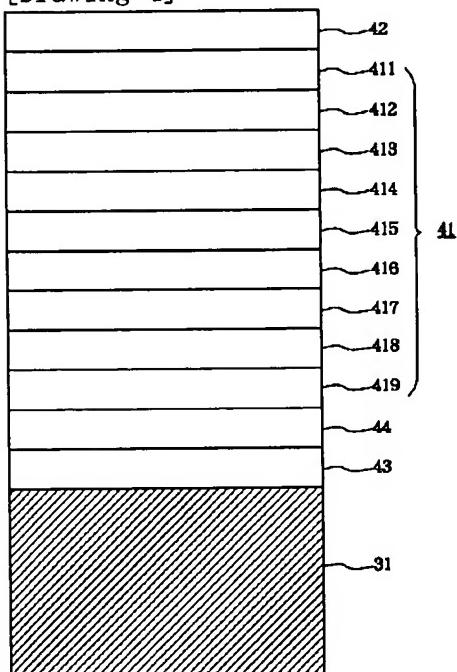
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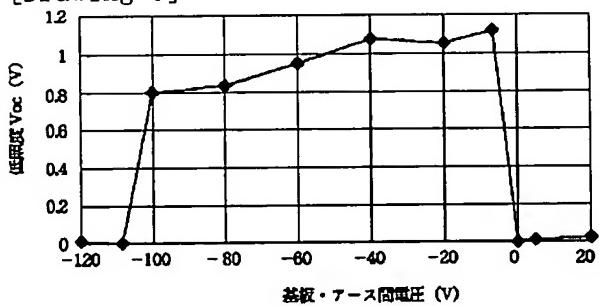
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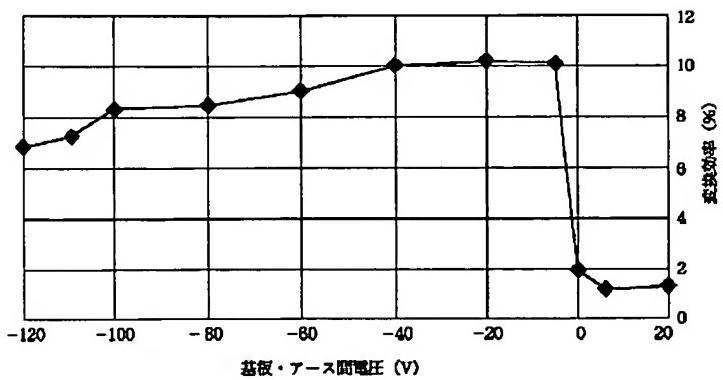
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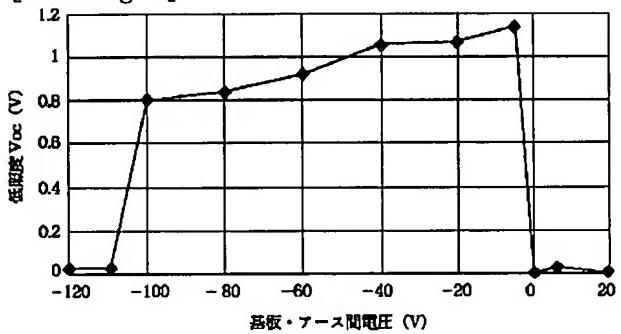
[Drawing 5]



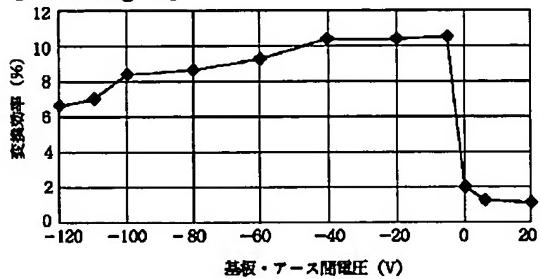
[Drawing 6]



[Drawing 7]



[Drawing 8]



[Translation done.]